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13. ABSTRACT (Maximum 200 words) <p>Three diaza-18-crown-6 ligands substituted with two each of 5-amino-2-hydroxybenzyl (1), 3-amino-5-chloro-2-hydroxybenzyl (2), or 3-amino-2-hydroxy-5-methylbenzyl (3) units (see Figure 1) were prepared as reported in our Technical Report No. 2 of August 13, 1998. Interaction of the ligands with Na⁺, K⁺, Ag⁺, and Cu²⁺ was evaluated by a calorimetric titration technique and the results are shown in Table 1. Heterobinuclear complexes were observed for complexes 2-Cu²⁺-Na⁺ and 3-Cu²⁺-Na⁺ with log K values of 1.86 and 1.41, respectively (see Table 1). These binuclear complexes are possible since the Cu²⁺ ion can interact with the neighboring amino and hydroxy groups of the two appended benzene rings leaving the macrocyclic cavity free for Na⁺. As expected, Cu²⁺-1, with the amino and hydroxy groups <i>para</i> to each other which does not allow a stable coordination array for Cu²⁺, did not form a binuclear complex with Na⁺. Possible structures for 2-Cu²⁺-Na⁺, 3-Cu²⁺-Na⁺, and 1-Cu²⁺ are shown in Figure 1.</p>				
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Technical Report No. 3

**Diaza-18-Crown-6 Ligands Containing Two Aminophenol Sidearms: New
Heterobinuclear Metal Ion Receptors**

by

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Table 1. Log K , ΔH (kJ/mol), and $T\Delta S$ (kJ/mol) Values for Interactions of Macrocyclic Ligands with Metal Ions in Methanol Solution at 25.0°C

ligand	cation	log K	ΔH	$T\Delta S$
1	Na ⁺	2.73 ± 0.06	-24.6 ± 0.7	-9.01
	K ⁺	2.81 ± 0.02	-34.8 ± 0.4	-18.8
	Cu ²⁺	> 5.5	-65 ± 3	> -33.6
2	Na ⁺	3.42 ± 0.04	-12.4 ± 0.7	7.12
	K ⁺	a		
	Ag ⁺	> 5.5	-47.9 ± 0.5	> -16.5
	Cu ²⁺	> 5.5	-68 ± 3	> -36.7
3	Na ⁺	3.00 ± 0.05	-7.9 ± 0.8	9.22
	K ⁺	2.36 ± 0.08	-10.6 ± 0.7	2.87
	Cu ²⁺	> 5.5	-69 ± 3	> -37.6
Cu ²⁺ -1	Na ⁺	a		
Cu ²⁺ -2	Na ⁺	1.86 ± 0.06	8.9 ± 0.4	19.5
Cu ²⁺ -3 ^b	Na ⁺	1.41 ± 0.05	17.8 ± 0.6	25.8

^aNo measurable heat other than heat of dilution indicating that ΔH or/and log K is small.

^bMeOH solutions of Cu²⁺-ligand (1:1) were titrated by a Na⁺-MeOH solution.

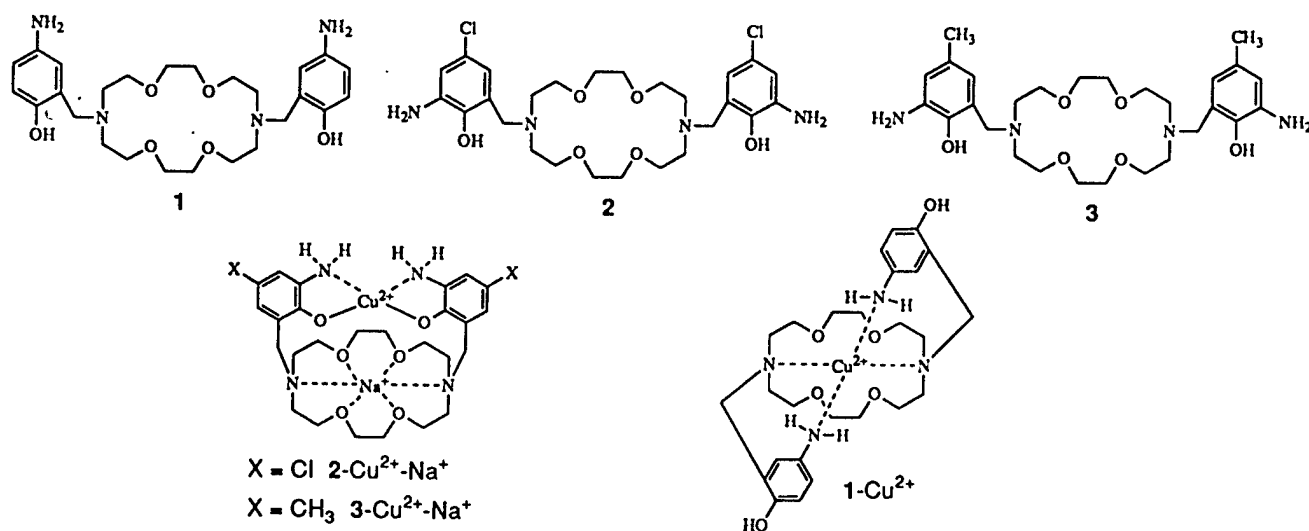


Figure 1.